

High volumetric capacitance near insulator-metal percolation transition

A. L. Efros*

*Department of Physics & Astronomy,
University of Utah, Salt Lake City UT, 84112 USA*

Abstract

A new type of a capacitor with a very high volumetric capacitance is proposed. It is based upon the known phenomenon of a sharp increase of the dielectric constant of the metal-insulator composite in the vicinity of the percolation threshold, but still on the insulator side. The optimization suggests that the metallic particles should be of nanoscale and that the distance between planar electrodes should be somewhat larger than the correlation length of the percolation theory and ≈ 10 to 20 times larger than the size of the particles while the area of the electrodes might be unlimited. The random electric field in the capacitors is found to be larger than the average field corresponding to the potential difference of electrodes. This random field is potentially responsible for dielectric breakdown. The estimated breakdown voltage of the new capacitor shows that the stored energy density might be significantly larger than that of electrolytic capacitors while the volumetric capacitances might be comparable. The charging and discharging times should be significantly smaller than corresponding times of batteries and even electrolytic capacitors.

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Creation of a capacitor with a very large capacitance per volume or weight (volumetric or weight capacitance) is an extremely important step on the way to a “green energetics”. Currently the leading role in this field belongs to the double-layer electrolytic capacitors also known as super- or ultra- capacitors. The main idea of the electrolytic capacitor is based upon a very narrow spatial gap between metallic electrode and electrolyte that plays the role of another electrode. The modern development, both experimental and theoretical can be found in the papers¹⁻⁴ and many others. The volumetric capacitance of these devices² might be about 85F/cm³

In this communication I propose a completely different approach to the problem of a supercapacitor that according to my estimates may successfully compete with the previous ones. The basis of the new approach is the sharp increase of the dielectric constant near the percolation threshold in a system of metallic nanoparticles distributed randomly in a dielectric matrix.

Suppose that the permittivity of the dielectric is $\epsilon_0 \kappa_D$, where ϵ_0 is the permittivity of vacuum, and κ_D is the dielectric constant. Suppose that x is a volume fraction of metal in the mixture. The insulator-metal transition of the percolation nature occurs at some critical value x_c . This critical fraction is practically independent of the form of the particles and $x_c \approx 0.15$ in three dimensional systems with a random distribution of metallic particles^{5,6}.

It has been shown by Dubrov, Levinshstein and Shur⁷ and by Efros and Shklovskii⁸ that on the dielectric side of the transition the dielectric constant κ of the composite material with the infinite volume diverges near the percolation threshold as

$$\kappa = \frac{\kappa_D}{\tau^q}, \quad (1)$$

$\tau = x_c - x > 0$, and q is a critical exponent. Note that Eq.(1) is only valid at $x_c - x \ll x_c$. A similar result was obtained later by Bergman and Imry⁹.

The origin of the exponent q is as follows. Consider a random composite of a dielectric with a small conductivity σ_D and metallic particles with a high conductivity σ_M such that $\sigma_M \gg \sigma_D$. One can introduce two different laws for the resulting conductivity:

$$\sigma(x) = \sigma_D / (x_c - x)^q \quad (2)$$

for $x < x_c$, and

$$\sigma(x) = \sigma_M (x - x_c)^t \quad (3)$$

for $x > x_c$. Eq. (2) is valid if $\sigma_D \ll \sigma(x) \ll \sigma(x_c)$, while Eq. (3) is valid if $\sigma_M \gg \sigma(x) \gg \sigma(x_c)$. A smooth transition from Eq.(2) to Eq.(3) occurs in a narrow region around x_c and⁸.

$$\sigma(x_c) = \sigma_M \left(\frac{\sigma_D}{\sigma_M} \right)^s. \quad (4)$$

It has been shown⁸ that the three exponents q, t, s are connected by one relation

$$q = t \left(\frac{1}{s} - 1 \right). \quad (5)$$

Eq.(1) for static dielectric constant has been obtained by considering the same problem at a finite frequency ω , doing analytical continuation⁸ in the upper half plane of a complex ω , and then putting $\omega = 0$. The exponent q in Eq.(1) is the same as in Eqs.(2,5)

There are some controversies concerning the numerical value of the exponent q in three dimensional (3D) case. The experimental result by Grannan *et al.*¹⁰ is $q = 0.73$. The same number is given in the review paper by Clerc *et al.*¹¹ that summarizes the results of different theoretical approaches. However, a similar review by Bergman and Stroud¹² gives $q = 0.76$. The last two results are close and in this paper I make a choice in favor of experimental data and the review¹¹, taking $q = 0.73$.

The sharp increase of the dielectric constant has been confirmed experimentally in a few other papers^{13,14}. In the experiment¹³ the dielectric constant increases about three order of magnitude reaching 10^5 near the percolation threshold of molybdenum particles in a ceramic. A similar result was reported by Pecharomman *et al.*¹⁵ in BaTiO₃ – Ni composite. In the percolative regime they got a high and frequency independent dielectric constant $\kappa \approx 80000$.

The physical reason of such increase is the existence of metallic clusters that have large but finite size. This size tends to infinity near the threshold. Almost all metallic sites of such a cluster belong to the “dead ends” which are connected to the rest of the cluster by one site only. The huge capacitance is created by the small distances between sites that belong to different metallic clusters, separated by polarized dielectric.

The percolation transition occurs when these clusters become connected and form the infinite cluster. The characteristic size of the finite clusters below the transition is of the order of the correlation length

$$L_c = l/\tau^\nu, \quad (6)$$

where l is the size of a metallic particle and ν is the exponent of the correlation length. In the 3D case $\nu \approx 0.87$ ^{16,17}.

Similar to Eq.(1), Eq.(6) is valid only at $x_c - x \ll x_c$. Note that both these equations and all equations obtained from them below are rather estimates because they should contain unknown numerical coefficients.

In a system of finite linear size the apparent divergence of the dielectric constant saturates at such small values of τ , when the correlation length L_c becomes of the order of this size. This result is common for all second-order phase transitions.

Consider a parallel plate capacitor with a large area S of the metallic plates and with a distance L between the plates. The capacitance $C = \epsilon_0 \kappa S / L$. Here κ itself increases with L at $L < L_c$. One can say that the dielectric constant near the percolation threshold has a spatial dispersion at $L < L_c$. At $L > L_c$ it is given by Eq. (1) and it is independent of L . Then the capacitance decreases with increase of L at $L \gg L_c$ as $1/L$. Thus, the optimal distance between the plates of a capacitor is $L \approx L_c$.

However, one should keep in mind that the percolation threshold x_c has a meaning for the infinite array only. Any set of samples with the same size L has a small critical region of $|x_c - x|$, where the threshold may appear with the probability about 1/2. The width of this region is^{5,6} of the order of $\delta = (l/L)^{1/\nu}$. To be sure that there are no electrical shorts between metallic electrodes one should work on the dielectric side outside the critical region at $\tau > \delta$. This means that $L > L_c$. Since the numerical factor in Eq.(6) is unknown and it may depend on the shape of metallic particles, I assume for the estimates that distance between electrodes is L_c as given by Eq.(6). To prevent electrical shorts every metallic electrode may be separated from infiltrated dielectric by a thin layer of a pure dielectric with a high electric strength.

In this approximation the capacitance per area C_S has the form

$$C_S = \epsilon_0 \kappa / L_c. \quad (7)$$

It is convenient to use a dimensionless length P such that $L_c = Pl$, where $P = \tau^{-\nu}$. Using Eqs.(1,6) one gets

$$C_S = \epsilon_0 \kappa_D (P)^{(q/\nu-1)} / l. \quad (8)$$

Following Clerc *et al.*¹¹ we assume that in a 3D array the ratio $q/\nu = 0.84$. Then

$$C_S = \epsilon_0 \kappa_D / (P)^{0.16} l. \quad (9)$$

An important characteristic of a capacitor is its volumetric capacitance. Assuming that

the distance between electrodes is L_c one gets for capacitance per volume

$$C_V = \epsilon_0 \kappa / L_c^2. \quad (10)$$

Using Eqs.(1,6) one gets

$$C_V = \epsilon_0 \kappa_D \left(\frac{L_c}{l} \right)^{q/\nu} L_c^{-2} \quad (11)$$

or

$$C_V = \epsilon_0 \kappa_D (P)^{(q/\nu-2)} / l^2. \quad (12)$$

Assuming $q/\nu = 0.84$ one gets

$$C_V = \frac{\epsilon_0 \kappa_D}{(P)^{1.16} l^2}. \quad (13)$$

The most striking result is that near the percolation threshold capacitances per area C_S and and per volume C_V *depend on the distance between metallic electrodes much more weakly than in the case of a regular dielectric.* Indeed, $C_S \sim 1/L^{0.16}$ instead of $C_S \sim 1/L$ in a regular dielectric while $C_V \sim 1/L^{1.16}$ instead of $C_V \sim 1/L^2$, where L is the distance between the plates of the capacitor. This gain in the capacitance results from the spatial dispersion of the dielectric constant κ , and it follows formally from Eq.(1) that has been substituted into Eqs.(7,10).

Now we see that close proximity to the percolation threshold is not the optimal solution because in this case L_c becomes larger and volumetric capacitance becomes smaller.

One should keep in mind, however, that the strong enhancement of the dielectric constant near the percolation threshold is valid if $L_c \gg l$ which also means that $P \gg 1$ and $\tau^{-1} \gg 1$.

The computational experience shows that in a 3D array it is enough to have $P \approx 15$ to 20. To find τ one should use $P = 1/\tau^\nu$.

Now I can do estimates. At $P = 20$ and $l = 1$ nm one gets

$$C_S \approx 0.55 \frac{\kappa_D}{100} \text{F/m}^2 \quad (14)$$

and

$$C_V = 27 \frac{\kappa_D}{100} \text{F/cm}^3. \quad (15)$$

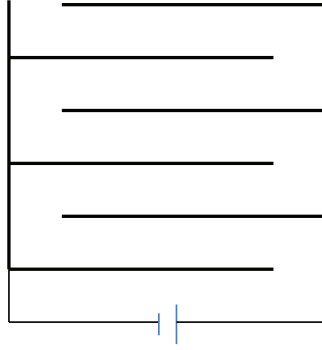


FIG. 1: Cross-section of a capacitor consisting of five thin capacitors connecting parallel. Straight thick lines show metallic electrodes. All space between them filled with dielectric infiltrated by metallic nanoparticles except thin preventing layer of a pure dielectric around each metallic electrode (see text). Thin lines show the battery connection to the capacitor. The openings between horizontal and vertical lines are shown large for clarity only. In fact, they should be large enough to prevent electrical shorts only.

Note that the value of κ_D in this estimate might be significantly larger than 100. For example recently¹⁸ $\kappa_D = 3000$ has been discovered in $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_3$ ceramics. Taking this value one finds that $C_V = 810\text{F}/\text{cm}^3$. Thus this estimate shows that the proposed capacitor might be comparable with the electrolytic one that provides $C_V = 85\text{F}/\text{cm}^3$.

The capacitor under discussion is very thin though the area of the metallic electrodes might be large. It is possible to make a capacitor of a cubic or of any other form with a parallel connection of the thin capacitors. An example of such a capacitor is shown in Fig. 1. It has almost the same volumetric capacitance as each thin capacitor.

Now I discuss the important issue of the maximum energy stored in the capacitor at a given capacitance. This energy is limited by the value of the voltage that can be safely applied to the capacitors without causing dielectric breakdown.

One can show that a capacitor made from a dielectric filled by metallic particles in the vicinity of the percolation threshold has a microscopic field \mathbf{e} of random orientation and much larger than the macroscopic field $E = U/L_c$, calculated from the applied voltage U .

Now I estimate the value of the field \mathbf{e} . The energy Q of the capacitor per unit surface area is

$$Q = C_S U^2 / 2. \quad (16)$$

On the other hand, this energy can be calculated microscopically as the energy of electric field \mathbf{e} per unit surface area of the capacitor

$$Q = \frac{\epsilon_0 \kappa_D}{2L_c^2} \int (\mathbf{e})^2 dV, \quad (17)$$

where the integral is taken over the cube L_c^3 , but the integrand is non-zero in the dielectric regions only because the field inside metals is zero. Note that Eq.(17) contains dielectric constant κ_D of a pure dielectric. Increase of the macroscopic dielectric constant κ and of the capacitance is due to the microscopic field \mathbf{e} . This field is the solution of the Poisson equation that takes into account metallic infiltration. Introducing the squared field averaged over the cube L_c^3

$$\langle (\mathbf{e})^2 \rangle = (1/L_c^3) \int (\mathbf{e})^2 dV, \quad (18)$$

one can write the energy of the capacitor Q per unit area in the form

$$Q = \frac{\epsilon_0 \kappa_D}{2} \langle (\mathbf{e})^2 \rangle L_c. \quad (19)$$

Comparing Eqs. (16,8), and (19) one gets

$$e \approx \sqrt{\langle (\mathbf{e})^2 \rangle} = \frac{U}{\sqrt{L_c l}} (L_c/l)^{(q/\nu-1)/2}. \quad (20)$$

Note that

$$e/E \approx (L_c/l)^{q/2\nu} \gg 1. \quad (21)$$

Strictly speaking the field e is inhomogeneous, but the inhomogeneity is not strong. The microscopic field and the large value of the permittivity near the percolation threshold are created by the dead ends of the finite clusters. The large capacitance can be understood in terms of the large areas covered by the dead ends of different finite clusters with different potentials. This coverage is dense so that the microscopic field should not be strongly inhomogeneous. Therefore I think that the fluctuations of the field e are not very important, and this field can be used to estimate the breakdown field.

One should also take into account that an electrical short between two finite clusters that appears due to a fluctuation means only that they become one cluster. Only multiple shorts may create the percolation between the electrodes that destroys the device.

To estimate the breakdown voltage U_b assume that the breakdown in the dielectric occurs due to tunnelling current which is usually the main reason at small distances¹⁹. The field

\mathbf{e} changes its direction at a distance of a few values of $l \approx 1\text{nm}$. Then the typical voltage drop inside the dielectric is of the order of

$$el = l \frac{U}{P^{(1-q/2\nu)}}. \quad (22)$$

The tunnelling current appears when the voltage drop given by the left hand side of Eq.(22) is equal to the gap width of the dielectric E_g (in volts). Due to the fluctuations of the field e it might be somewhat less than E_g , say $E_g/\sqrt{2}$. Then from Eq.(22) one gets

$$U_b = \frac{E_g}{\sqrt{2}} P^{(1-q/2\nu)}. \quad (23)$$

At $P = 20$ and $E_g = 3\text{V}$ the maximum voltage that can be applied is $U_b = 12\text{V}$.

These calculations reveal another important advantage of the proposed capacitor. The breakdown voltage is larger than $E_g/\sqrt{2}$ in volts. Note that the random field e that creates breakdown is larger than the average field E , but the tunnelling distance l is so small that the voltage drop el is smaller than potential difference U that is applied to a capacitor (See Eq.(22)).

Now we can estimate the maximum density of the stored energy W as

$$W = \frac{C_V U_b^2}{2}. \quad (24)$$

Using Eqs(12,23) one gets

$$W = \frac{9}{4} \frac{\epsilon_0 \kappa_D}{l^2} (E_g/3V)^2. \quad (25)$$

This equation does not contain any critical exponents. If $E_g = 3\text{V}$, $l = 1\text{nm}$, one finds $W = 0.55(\kappa_D/100)\text{Wh/cm}^3$. This is a very large volumetric energy. For the electrolytic capacitors the energy per weight is about 5 Wh/kg (See¹). This happens because the breakdown voltage in a double-layer electrolytic capacitor is only (2 to 3)V.

Note that the charging and discharging times of the proposed capacitor should be much smaller than the corresponding times of batteries and even smaller than times of electrolytic capacitors. The reason is that both batteries and electrolytic capacitors operate with the ion currents. In the proposed capacitor only the time of polarization of the dielectric is relevant.

One can think that due to the metal infiltration the leakage current in the proposed capacitor should be larger than in a regular dielectric based capacitor. In principle, this

is true, but the effect is not strong. The conductivity of the infiltrated system near the percolation threshold is given by Eq.(4). It follows from Eq.(5) that $s = 0.72$. Then

$$\sigma(x_c) = \sigma_D^{0.72} \sigma_M^{0.28}. \quad (26)$$

Thus, the influence of metallic particles is not strong. This might be the reason why Pecharroman and Moya¹³ claimed a low leakage current in their experiment.

In summary, as follows from my estimates, dielectric media with metallic nanoparticles that are near the percolation threshold might be promising materials for capacitors with large volumetric capacitance and large stored energy density. The material parameters I use for the estimates are far from exceptional. They do not correspond to a single specific material. I think that success or failure of the whole idea depends on the proper choice of the dielectric material. The most important requirements are high dielectric constant and possibility of infiltrating by metallic nanoparticles using an advanced nanotechnology. The requirement for the gap E_g depends on whether one needs high voltage or low voltage capacitor. If volumetric capacitance is large enough, the stored energy density might be large in both cases.

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* Electronic address: efros@physics.utah.edu

¹ P. Simon and Y. Gogotsi, *Nature Materials* **7**, 845 (2008).

² C. Largeot, C. Portel, J. Chmiola, P.-L. Taberna, Y. Gogotsi, and P. Simon, *J. Am. Chem. Soc.* **69**, 2730 (2008).

³ B. Skinner, M. S. Loth, and B. I. Shklovskii, *Phys. Rev. Lett.* **104**, 128302 (2010).

⁴ M.S.Loht, B. Skinner, and B. I. Shklovskii, *Phys. Rev. E* **82**, 056102 (2010).

⁵ B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, 1984), chapter 5.

⁶ A. L. Efros, *Physics and Geometry of Disorder* (Mir, Moscow, 1986), chapter 9.

⁷ V. E. Dubrov, M. E. Levinshtein, and M. S. Shur, *Sov. Phys.JETP* **43**, 1050 (1976).

⁸ A. L. Efros and B. I. Shklovskii, *Phys.Status. Solidi* **76**, 475 (1976).

⁹ D. Bergman and Y. Imry, *Phys. Rev. Lett* **39**, 1222 (1977).

- ¹⁰ D. M. Grannan, J. C. Garland, and D. B. Tanner, Phys. Rev. Lett **46**, 375 (1981).
- ¹¹ J. Clerc, G. Giraud, J. M. Laugier, and J. M. Luck, Adv.Phys. **39**, 191 (1990).
- ¹² D. J. Bergman and Stroud, *Solid State Physics*, vol. 46 (Academic Press inc., 1992).
- ¹³ C. Pecharroman and J. S. Moya, Adv. Materials **12(4)**, 294 (2000).
- ¹⁴ M. Valant, A. Daksobler, M. Ambrozic, and T. Kosmac, J. European Ceramic Soc. **26**, 891 (2006).
- ¹⁵ C. Pecharroman, F. Esteban-Betegon, J. F. Bartolome, S. Lopez-Esteban, and J. S. Moya, Adv.Materials **13**, 1541 (2001).
- ¹⁶ D. Stauffer and A. Aharony, *Introduction to percolation theory* (Taylor&Francis, 1992), p. 52.
- ¹⁷ M. Sahimi, *Applications of percolation theory* (Taylor&Francis, 1990), p. 16.
- ¹⁸ C. Liu, P. Liu, J. ping Zhou, Y. He, L. na Su, L. Cao, and H. wu Zhang, J. Appl. Phys. **107**, 094108 (2010).
- ¹⁹ H. C. Lin, P. D. Ye, and G. D. Wilk, Appl. Phys. Lett **87**, 182904 (2005).